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    THE PURPOSE OF THIS WORK IS TO PROVIDE TECHNICAL INFORMATION NECESSARY TO EVALUATE THE APPLICABILITY, ANTICIPATED PERFORMANCE, AND EFFECTIVENESS OF REMEDIAL ALTERNATIVES BEING CONSIDERED FOR RMA. THE DATA OBTAINED AND THE EVALUATIONS PERFORMED ON THIS DATA SHOULD BE VALUABLE IN THE DETERMINATION OF WATER QUALITY IMPACTS RESULTING FROM CONTAMINATED SOIL LEFT BELOW THE SEASONAL HIGH WATER TABLE. THIS DATA WOULD ALSO BE USED IN PREDICTING THE REDUCTIONS IN CONTAMINANTS IN GROUND WATER CONCENTRATIONS THAT WOULD RESULT FROM THE REMOVAL OF CONTAMINATED SOIL.
    THE OBJECTIVE OF THE WORK EFFORT DESCRIBED IN THIS TECHNICAL PLAN IS TO EXAMINE PARTITIONING OF PRIMARY SECTION 36 CONTAMINANTS BETWEEN SOIL AND GROUND WATER. THE METHODOLOGY DESCRIBED INCLUDES THE DETERMINATION OF DISTRIBUTION COEFFICIENTS (KD) AT SPECIFIED SECTION 36 LOCATIONS.

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LITIGATION TECHNICAL SUPPORT AND SERVICES

ROCKY MOUNTAIN ARSENAL

TECHNICAL PLAN

DETERMINATION OF PARTITION COEFFICIENTS FOR THE PRIMARY
CONTAMINANT SOURCES OF SECTION 36

TASK NUMBER 23

OCTOBER 1986

ENVIRONMENTAL SCIENCE AND ENGINEERING, INC.

PROGRAM MANAGER'S OFFICE FOR ROCKY MOUNTAIN ARSENAL

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TECHNICAL PLAN
DETERMINATION OF PARTITION COEFFICIENTS
FOR THE PRIMARY CONTAMINANT SOURCES OF SECTION 36

PURPOSE

The purpose of this work is to provide technical information necessary to evaluate the applicability, anticipated performance, and effectiveness of remedial alternatives being considered for RMA. The data obtained and the evaluations performed on these data should be valuable in the determination of water quality impacts resulting from contaminated soil left below the seasonal high water table. These data would also be used in predicting the reductions in contaminants in ground water concentrations that would result from the removal of contaminated soil. This type of evaluation is necessary to conceptually design a ground water extraction system and to identify the length of time such a system must operate to meet water quality criteria.

The objective of the work effort described in this technical plan is to examine partitioning of primary Section 36 contaminants between soil and ground water. The methodology described below includes the determination of distribution coefficients (K_d) at specified Section 36 locations. Although this initial work effort is a small scale investigation, the results of this work should allow: 1) modification or refinement of the K_d methodology for application on an arsenal wide basis; 2) determinations of an anticipated range of K_d values for contaminants of concern; 3) comparison of the measured range of K_d values with values found in the literature; and 4) a preliminary evaluation of variability in K_d values with such factors as distance from the primary source, aquifer mineralogy, and soil geochemistry.

To test the validity of the use of distribution coefficients to evaluate contaminant distribution, three areas in Section 36 of RMA have been identified for preliminary investigation. These areas were selected based on the results of the Phase I Remedial Investigation. The three areas are those that exhibit the highest contaminant concentrations observed in Section 36, and appear to be primary contaminant sources that are inducing

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contaminant migration via the local ground water system. These contaminant sources include Basin A (36-1), the Lime Settling Pits (36-4), and the Insecticide Pits (36-3).

THEORY

To estimate reductions in ground water concentrations that would result from the various remedial options, a knowledge of how various RMA contaminants are distributed between soil and water, and how this distribution may change with time, source concentration, and aquifer properties must be obtained.

Geochemical reactions or processes which may affect the mobility of inorganic and organic contaminants include solubility, complexation, and adsorption/desorption. Complexation may occur with dissolved organic matter (DOM) or with inorganic species. Adsorption/desorption reactions may occur with both inorganic aquifer minerals or with organic matter that is present in colloidal form or as coatings on mineral grains. The evaluation of partitioning is further complicated in the RMA soil/water system by the existence of a complex matrix of organic and inorganic contaminants.

As it is not possible nor realistic to evaluate the influence that each of the above mechanisms has on the partitioning of contaminants between soil and water, a more simplistic investigative approach is commonly adopted for system evaluations. This approach is to measure a distribution coefficient (K_d) for each contaminant of concern. This K_d is most commonly defined as:

$$K_d = \frac{S \; (ug/g)}{C \; (ug/g)}$$

where:

- o   S is the sorbed concentration of the contaminant in soil in units of ug/g;

- o   C is the concentration of the contaminant in water in units of ug/g; and

- o K_d is unitless. Values for K_d are usually determined in the laboratory with batch or column experiments but can also be measured for field conditions.

The mass balance for the total, aqueous, and sorbed concentrations for each constituent can be represented by the following equation:

$$\rho T = \theta C + \rho S \qquad (2)$$

where:

o ρ is the soil bulk density in kilograms of oven dry soil per liter of volume;

o θ is the volumetric soil/water fraction in kilograms of water per liter of volume; and

o T is the total concentration of the specific constituent (water and soil) in the sample per kilograms of dry soil.

Combining and rearranging equations 1 and 2 yields:

$$T/C - \theta/\rho = K_d \qquad (3)$$

θ is equal to ρM, where M is the soil water content by weight in kilograms of water per kilogram of oven dry soil. Rearranging equation 3:

$$K_d = T/C - M \qquad (4)$$

Therefore, a K_d value can be obtained by using equation (4) and knowing soil water content, total soil-water system concentration for the constituent, and the aqueous concentration of the same constituent.

The primary advantage of utilizing K_d values for projecting changes in ground water contaminant concentrations is that K_d values can be relatively easily determined and are also easily applied in geochemical evaluations. However, caution must be applied in the determination and use of K_d values for estimation of contaminant partitioning. Distribution coefficients are only strictly valid for conditions under which they are measured. If a K_d value is determined for conditions in a contaminant source, this value may not be valid for the downgradient aquifer system. This may be due to differences in soil composition, changes in contaminant concentration, alterations in the Eh-pH conditions of the system, or changes in other aqueous properties such as ionic strength. Although many organic contaminants exhibit linear or Freundlich (constant partitioning) isotherms large variations in contaminant concentrations can result in deviation from

anticipated behavior. Such conditions typically exist downgradient of a contaminant source. In spite of the disadvantages and cautions which must be exercised in their use, the determination of K_d values for the RMA system is the preferred method for the estimation of contaminant availability and transport.

Realistically it will not be possible to assign a single K_d value to each contaminant source and its immediate downgradient area. This test program will attempt to measure a working range of K_d values. Ideally, data collection points should be located within, and at several locations downgradient, of each source. In this manner, variability in K_d values may be evaluated as a function of contaminant concentration, overall solution composition, and the geochemistry of the aquifer material. However, rough preliminary calculations suggest that some soil concentrations for very soluble compounds may be at levels below analytical detection limits in aquifer soils. As a result, this investigation has been designed to collect soil and water samples from a limited number of locations where contaminants are most likely to occur at detectable concentrations in both water and soil.

Evaluation of the data from this initial program will provide guidance for subsequent investigations, including evaluation of remedial alternatives as well as additional field and/or laboratory determinations of K_d values for other locations. Subsequent determinations of representative K_d values for additional contaminant sources and contaminated downgradient areas may be required following analysis of the data from this investigation. The data may indicate a range of K_d values for each source area and contaminant matrix as a result of variations in solution and aquifer compositions. If investigative activities show a narrow range of distribution coefficients for a specific contaminant, then a high degree of confidence can be placed in calculations that estimate rates of downgradient transport for the sources studied. If K_d values are widely divergent, a lower degree of confidence must be placed in the resultant calculations and estimations, especially if variations in K_d values do not follow any discernable pattern.

Upon the completion of this initial K_d study, the values obtained from field samples will be compared to literature K_d values. These literature values have been determined primarily from laboratory studies. It is anticipated that future K_d studies will be necessary in other RMA source areas and contaminant plume regions. Other work efforts which should be considered following evaluation of the data from this study would be desorption experiments by either batch or column methods using RMA soils and "background" or "uncontaminated" quality water to determine reversibility of contaminant adsorption. Additional laboratory adsorption/desorption studies may be necessary to evaluate rigorously the influence that various soil or water parameters have on the rates and concentrations of adsorption/desorption reactions. These additional tests would be set up as column experiments. Such experiments would utilize a "clean" RMA soil and introduce contaminated ground water until equilibrium is achieved, followed by desorption with "background" quality water.

METHODS OF K_d DETERMINATION

Distribution coefficients can be estimated from field samples in several ways. Each method has a unique set of advantages and disadvantages that must be considered when evaluating these data.

One method of determining partition coefficients for RMA contaminants is to obtain a representative soil sample from a specific subsurface saturated interval and then install a ground water monitoring well in the same borehole with the screened interval located where the soil sample had been obtained. When the soil sample is obtained, free water can be allowed to drain off, but care should be taken not to lose fine-grained particulate matter as this material with its high specific surface area may contain a large proportion of the sorbed contaminants. Once in the laboratory, additional free water can be removed from the sample by centrifugation. Contaminant concentrations in the soil will be determined per certified USATHAMA methods. Two alternatives are available for obtaining the aqueous concentration. One method is to analyze the centrifuged porewater for contaminants. Special care must be taken during sample handling to preserve the volatile organic compounds. A second option for obtaining the aqueous

concentration of each constituent is to sample ground water from the
monitoring well after proper installation, development, and purging. The
ground water sample is then analyzed for contaminants.

Errors included in K_d values generated by these sampling methods and through
use of equation 1 should be small for contaminants which are strongly
partitioned to the soil phase. The errors will be small because low
concentrations of contaminants in residual water left in the soil sample
will not significantly influence the total concentration of the soil. For
contaminants that partition strongly to the aqueous phase, the presence of
residual water containing high contaminant concentrations may result in
anomalously high measured soil concentrations. If the mass of contaminants
contained in residual water is significant, soil concentrations can be
adjusted using moisture content determined in the soil sample following
centrifugation. The mass of contaminant in residual water retained in the
sample may be estimated from ground water analyses and then be subtracted
from the mass determined in the moist soil sample in order to estimate the
true concentration in the dry soil. A comparison of conductivity in the
extracted pore water with the conductivity of the corresponding ground water
sample will provide a rough indication of the relative similarity in
composition between pore and ground water samples.

Equation 4 may be used to adjust for the effects of residual pore water and
to directly determine K_d for field conditions. The total concentration, T,
should be measured for the centrifuged soil sample. The water content, M,
is also measured on this centrifuged sample. The aqueous concentration, C,
is obtained by sampling of the newly installed monitoring well. As this
method is considered to be the best of several available methods, Section 36
samples will be subjected to this procedure.

Upon evaluation of field K_d data and requirements of the Feasibility Study,
it may be necessary to also determine K_d values under laboratory conditions.
Methods for determination of distribution coefficients in the laboratory
include column and batch investigations. Column tests require measurement
of elution times and contaminant concentrations in a solution which has been

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passed through a chromatographic column packed with the soil of interest.
Batch tests involve equilibrating known volumes of water and soil spiked
with a known quantity of contaminant in a closed container and directly
measuring partitioning between the two phases. These laboratory methods
provide a controlled environment in which to measure sorptive effects.
Unfortunately, research has indicated considerable difficulty in applying
laboratory measurements of K_d's to simulations of field contamination
problems. Foremost among these problems are the collection and preparation
of samples for investigation. Efforts to homogenize and prepare samples for
laboratory tests result in alteration of the soil structure and
stratification. Alteration of these soil structures through disaggregation
or compaction results in an experimental substrate which does not adequately
reflect field conditions.

Although these laboratory derived distribution coefficients are not directly
applicable to field simulations, leach tests may be performed to evaluate
the reversibility of adsorption and to provide independent estimates of K_d.
Following interpretation of the data from the proposed field program, the
necessity of additional laboratory investigations will be re-evaluated.

ADDITIONAL GEOCHEMICAL TESTING

To aid in the evaluation of contaminant partitioning, the measurement of
several additional properties of the water and soil are recommended.
Enhanced contaminant transport may result from either organic or inorganic
complexation in the aqueous phase. Proposed aqueous determinations include
characterization of the basic inorganic chemistry of the water, including
analysis of:

- o   Major cations and anions;
- o   Specific conductance;
- o   Temperature;
- o   pH; and
- o   Redox potential (DO or platinum redox electrode).

In addition to inorganic characterization of the water, measurement of dissolved organic carbon (DOC) should also be performed.

Properties of the aquifer material which have been shown to influence sorptive behavior include clay content and mineralogy, iron and manganese content, surface area and organic matter content. Proposed soil determinations include:

- o Mineralogic analysis of bulk sediment and clay separates by X-Ray diffraction;
- o Elemental composition by X-Ray Fluorescence;
- o Specific surface area by (BET) nitrogen adsorption;
- o Particle size distribution by sieve and hydrometer analysis;
- o Organic matter content by Walkley Black method; and/or Leco furnace;
- o Water content by drying; and
- o Iron and manganese oxide content by weak acid extraction.

Determination of these additional geochemical parameters will allow correlation of K_d values with bulk aqueous chemistry and sediment characteristics which influence sorptive behavior. These correlations may provide significant insight to the parameters controlling contaminant partitioning. It is anticipated that soil organic matter will strongly influence transport of organic contaminants.

Local laboratories are proposed for these analyses to eliminate costly and time consuming certification procedures. Although these results will not be USATHAMA certified, they will be of adequate precision and accuracy to allow correlation with K_d results.

## K_d INVESTIGATIONS AT SOURCES 36-1, 36-3, AND 36-4

The investigative strategies at all three contaminant source areas are similar and therefore will be discussed collectively. All samples generated by this study will be subjected to identical analytical procedures.

Five locations have been selected for collection of saturated zone samples
and subsequent completion as monitoring wells as shown in Figure 1. These
locations were selected on the basis of elevated contaminant concentrations
in samples collected above the water table during the Phase I boring
program. Several locations were selected to be hydrologically downgradient
of soils exhibiting high contaminant concentrations. Two of the proposed
locations are situated within Basin A (Source 36-1) near a channel which
runs through the center of the basin. Two of the proposed locations are in
the vicinity of the Insecticide Pits (Source 36-3). One location is located
in the center of Source 36-3 and another is sited immediately downgradient
of the source boundary. The final proposed location is located on a berm
adjacent to the Lime Settling Pits (Source 36-4).

The preferred drilling method for obtaining representative soil samples is
the hollow-stem-auger continuous-coring system currently in use at RMA.
Continuous sampling will be performed at depths where the screen is to be
set and one foot sections of the core will be submitted for analysis.
Intervals to be analyzed will be selected in the field after visual
inspection of the core. Intervals exhibiting variations in grain size and
color will be represented among the samples analyzed. Saturated samples will
be retained in polybutyrate liners during shipment to the laboratory. At
least three soil samples will be collected within the projected screened
interval. Screened intervals will have a maximum length of five feet.
Polybutyrate liners will be handled, packaged, and shipped according to
procedures followed under other RMA tasks and described in the Task 1
Technical Plan. Samples will be handled to minimize water loss.

Upon receipt of samples by the laboratory, free pore water will be removed by
ultracentrifugation. Water content of the ultracentrifuged solid phase will
be measured. Following ultracentrifugation, the soil samples will be
analyzed for the suite of RMA contaminants including:
- o   Purgeable halocarbons;
- o   Purgeable aromatics;
- o   Organochlorine pesticides;
- o   Organosulfur compounds;
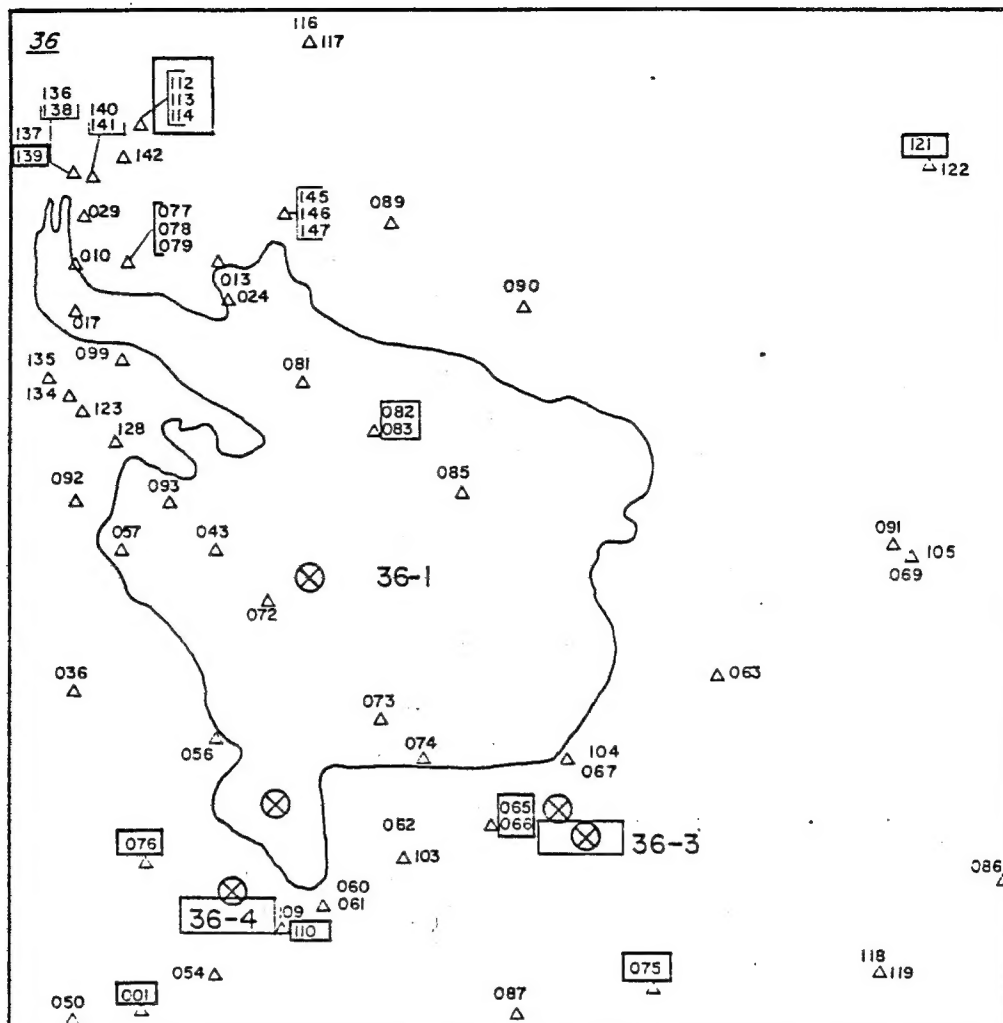
KEY

△ 000 Task 4 wells in section 36 used for chemical sampling and water level measurements

△ ⬚ Ⅲ Wells sampled for chemical analysis 3rd and 4th Quarters

⊗ Proposed Kd well locations

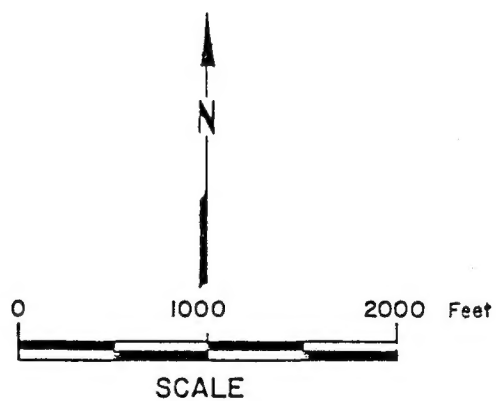Figure 1
PROPOSED Kd WELL LOCATIONS

Prepared for:
U.S. Army Program Manager's Office
For Rocky Mountain Arsenal
Aberdeen Proving Ground, Maryland

o   DIMP/DMMP;

o   DBCP;

o.   DCPD; and

o   Metals (As, Hg, Cu, Pb, Zn, Cr, Cd).

Extreme care will be taken to perform ultracentrifugation and sample
extractions as quickly as possible to prevent loss of volatile organics
prior to analysis. Replicate subsamples will be removed from each of two
core samples submitted for analysis. These subsamples will be analyzed
independently to provide an indication of small scale variability in
contaminant concentrations.

Upon completion of drilling and sampling efforts a single ground water
monitoring well will be installed at each location.   Five foot screen
lengths are proposed for each K_d well installed. This relatively short
screened interval will minimize the variability in aquifer soil properties
associated with each corresponding ground water sample. Although exact
screen placement will be determined in the field, the screened intervals are
anticipated to be located immediately below the water table in relatively
permeable sediments. The wells will be installed to USATHAMA specifications
and adequately developed by pumping. Following the required time delay
(14 days), the well will be purged until geochemical parameters
(pH, specific conductivity, temperature, dissolved oxygen, redox potential)
have stabilized. After stabilization, an adequate volume of water will be
collected in the appropriate bottles using the necessary preservation
techniques to subject waters to analysis for:

o   Purgeable halocarbons;

o   Purgeable aromatics;

o   Organochlorine pesticides;

o   Organosulfur compounds;

o   DIMP/DMMP;

o   DBCP;

o   DCPD;

o   Metals (As, Hg, Cu, Pb, Zn, Cr, Cd);

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o   Cations (Na, K, Mg, Ca); and

o   Anions (HCO_3/CO_3, Cl, SO_4, F, NO_3).

One well will be selected for collection and analysis of replicate ground water samples. These replicate samples will be collected over a period of one week to ensure that the samples are representative of stabilized ground water conditions.

Concentrations measured by this activity will be utilized as aqueous concentrations, C, for the determination of K_d values for each detectable contaminant. Therefore, this study should have obtained both total saturated soil and related water concentrations for detectable contaminants and K_d values can be calculated. It is anticipated that for some samples, concentrations of specific contaminants may be undetectable and therefore no K_d values can be determined. Values for partition coefficients will be evaluated with respect to other soil properties and distance from the contaminant source to identify, if possible, the changes in K_d related to these variables. Specific data analyses and future use of the K_d values will be determined on a compound by compound basis after the data are available. Therefore, this process will not be discussed here but will in all probability involve the use of a range of (minimum and maximum or mean) K_d values for each contaminant.

Variability in distribution coefficients will be evaluated, compared to the other soil and water parameters determined and also compared to literature K_d values. Resultant K_d values will be correlated with specific surface area, organic carbon content, aquifer mineralogy, elemental composition, particle size distribution and dissolved organic carbon. This supporting data should be invaluable for aiding in the interpretation of partition coefficient data and may shed light on variations observed for different soil-water system conditions.

LITIGATION TECHNICAL SUPPORT AND SERVICES

ROCKY MOUNTAIN ARSENAL

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